

REDUCTION OF HALOFORMS IN DRINKING WATER SUPPLIES

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Ministry
of the
Environment

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REPORT # 69

REDUCTION OF HALOFORMS IN DRINKING
WATER SUPPLIES

by:

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Water Technology Section
Pollution Control Branch
Ontario Ministry of the Environment

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Summary

A bench-scale study on water from Belleville, Brantford, Cayuga and the Humber River in Ontario was conducted to determine the minimum modifications of existing water treatment processes that can reduce the formation of haloforms in Ontario drinking water supplies.

The experiments examined included:-

- (1) removal of haloform precursors (post-chlorination)
(a) with coagulation using various types of coagulant chemicals; (b) with adsorption on granular activated carbon (GAC); (c) by the use of powdered activated carbon (PAC).
- (2) removal of haloforms (pre-chlorination) with the same three techniques.

All analyses for chloroform and other haloforms were performed by the Direct Aqueous Injection (DAI) Method.

The results showed that coagulation with alum and activated silica before chlorination was effective in reducing the haloform precursors by 92%.

By moving the point of chlorination to follow alum coagulation/sedimentation, the concentration of haloforms in the treated water was further decreased by 100%.

Ozone, potassium permanganate and hydrogen peroxide were tested as possible alternatives to chlorine in the pre-treatment process. Ozone did not alter the effectiveness of haloform precursor removal in the subsequent coagulation and sedimentation treatment. Potassium permanganate affected the overall performance of alum coagulation (with and without activated silica) in haloform precursor removal while hydrogen peroxide significantly altered the overall

performance of alum coagulation (without activated silica) only.

Powdered activated carbon was not effective in reducing the haloform precursors or haloforms after they were formed. Granular activated carbon was found to be effective in reducing haloform precursors by up to 90%.

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1. INTRODUCTION

Chloroform and other haloforms have been detected in varying concentrations in drinking water supplies as a result of chlorination, a conventional practice for the disinfection of drinking water.^(1,2) Naturally occurring humic substances which often produce colour in raw water supplies have been identified as some of the organic compounds which have combined with chlorine to form the haloforms.⁽³⁾ Chloroform, bromodichloromethane and dibromochloromethane were found to be at predominant levels among the haloforms formed.⁽⁴⁾

These haloforms are suspected carcinogens with possible health hazard implications. A report of the U.S. National Cancer Institute dated March 1, 1976,⁽⁵⁾ states conclusively that chloroform may now be categorized as a carcinogen. The release of this report set off a wave of reaction and the U.S. Food and Drug Administration moved to prohibit further use of chloroform in drug, cosmetic and food packaging products effective on July 8, 1976.⁽⁶⁾ To date, there is no prescribed limit established for haloforms in drinking water, but a Maximum Contaminant Level of 0.10 milligrams per litre for Total Haloforms in drinking water for systems serving populations of more than 75,000 was proposed by the U.S. Environmental Protection Agency (EPA), in January 1978.

Several approaches have been attempted in minimizing the concentration of chloroform and other haloforms in drinking water,⁽⁷⁾ such as; to remove the haloforms after they were formed; to prevent their formation by removing the precursors of the haloforms before chlorination; or to use an alternate disinfectant including ozone, chlorine dioxide, UV/ozone and ferrates (Iron VI).⁽⁸⁾ These approaches are still under investigation by different groups of scientists and engineers in North America as well as in Europe.

In a recent publication, the U.S. EPA has indicated that lower concentrations of haloforms are formed if chlorine is added to water of the highest quality and with the lowest possible organic content⁽⁹⁾. Low haloform concentrations can be effectively maintained in the treated water by reducing the concentration of haloform precursors before chlorination. Since many organic compounds can be effectively removed from water by adsorption on activated carbon,⁽¹⁰⁾ producing high quality water with low organic content, the chloroform precursors could possibly be reduced by adsorption on activated carbon before chlorination.

The chloroform precursors are considered to be organic substances that could be complexed with alum or other coagulants and precipitated with the floc.⁽¹¹⁾ By coagulation and sedimentation, some of the organics could be reduced to a lower level prior to chlorination. The point of chlorination therefore becomes significant in minimizing the formation of haloforms in finished water.

In December 1975, a laboratory scale investigation on water from Belleville, Brantford, Cayuga and the Humber River was initiated to determine the minimum modifications to existing water treatment processes that can reduce the formation of haloforms in Ontario drinking water supplies. The experiments examined included:-

- (1) the removal of haloform precursors (using the following techniques), (a) with coagulation using various coagulant chemicals; (b) with adsorption on granular activated carbon (GAC); (c) by the use of powdered activated carbon (PAC), all with chlorination only in the post position.
- (2) the removal of haloforms after they are formed during pre-chlorination, by the same three techniques.

A survey for monitoring the levels of haloforms in Ontario drinking water supplies was initiated in 1974 and has been continued since then.⁽¹²⁾ Chloroform

has been the only haloform found in any significant quantity. Bromodichloromethane and dibromochloromethane have generally been found at levels less than 10% of the total haloforms measured. Three municipal waters in Ontario, Belleville, Brantford and Cayuga were found to have the highest chloroform levels at 241 $\mu\text{g/l}$, 250 $\mu\text{g/l}$ and 256 $\mu\text{g/l}$ respectively. These water supplies were then selected for intensive studies on the reduction of haloforms.

The Ministry has been using the Direct Aqueous Injection (DAI) method for the analysis of haloforms. Water samples to be analyzed are injected directly into a gas chromatograph (GC) without any special handling or pre-treatment on the samples. However, the Purge method which is proposed to be used by the U.S. EPA, requires the purging of the volatile organics from water with an inert gas (usually helium) and trapping them in a short column packed with a porous polymer, from which it is thermally eluted into a gas chromatograph. The DAI method is faster than the Purge method and measures the "Total Potential Haloforms"⁽¹³⁾. Values obtained from this method tends to be higher than the Purge method which measures the "Free Haloforms". The DAI method is measuring about 1.7, 2.0 and 3.3 times as much chloroform, bromodichloromethane and dibromochloromethane respectively as that which will be obtained from the Purge method.

Results of this study are evaluated in terms of the reduction of the potential for haloform formation with post-chlorination only and the reduction of potential haloform with pre-chlorination.

2. DESCRIPTION OF WATER TREATMENT PLANTS

2.1 Belleville Water Treatment Plant

The Belleville Water Treatment Plant receives its water from the Bay of Quinte via a 427 metre (1400 feet) long, 760 mm diameter (30 inches) intake pipe.

Slight variations in alkalinity, colour, turbidity, TOC and pH of the raw water were measured throughout the year and the results of the analyses of the raw water are shown in Table 1.

The treatment system consists of physical and chemical treatment processes and is shown in Figure 1. The plant's capacity is 34,000 m³/d (9 MGD) serving a population of 35,000. Alum is dosed at 30 mg/l; the average chlorine dose is 4.2 mg/l with a total chlorine residual of 0.8 to 1.0 mg/l in the distribution system.

2.2 Brantford Water Treatment Plant

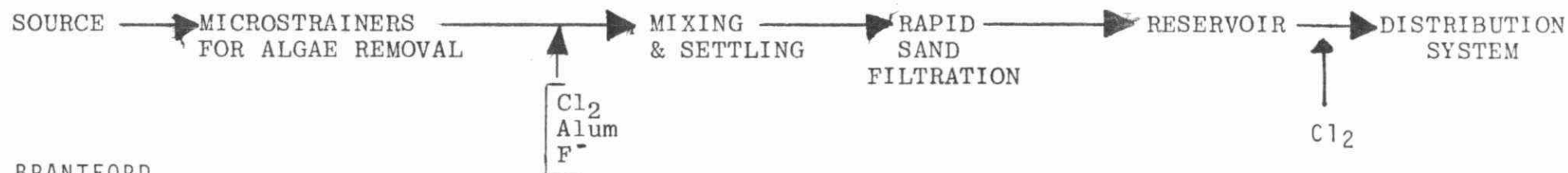
Brantford Water Treatment Plant obtains raw water from the Grand River via the Holmedale Canal. The Grand River receives considerable industrial and municipal waste inputs discharged upstream of the water treatment plant. Turbidity, colour, TOC, pH and alkalinity of the water samples taken from the Grand River during the study period from November, 1975 to September 1977 vary slightly. The analysis of the raw water is shown in Table 1.

The treatment process consists of pre-chlorination, screening, air mixing in pre-treatment tanks (during winter months only), the addition of powdered activated carbon, pre-ammoniation (when necessary), sulfuric acid-activated silica, alum and lime, flash mixing, flocculation, coagulation, sedimentation, filtration, the addition of sodium silico-fluoride and sulfonation or post-chlorination and ammoniation prior to being pumped to the distribution system. The process schematic is shown in Figure 1.

The plant is operating at 49% of its nominal capacity of 68,130 m³/d (18 MGD). The average dosage of chlorine is 9.8 mg/l with a free chlorine residual of 3 to 4 mg/l before entering the pre-treatment basin. Powdered activated carbon is used for taste and odour; the average dosage of powdered activated carbon used is 1.8 mg/l. The average dosages of alum and activated

FIGURE 1 SCHEMATIC DIAGRAMS OF THE
TREATMENT PROCESSES AT BELLEVILLE,
BRANTFORD AND CAYUGA WATER TREAT-
MENT PLANTS

BELLEVILLE



BRANTFORD



CAYUGA



TABLE 1 RAW WATER QUALITIES

SOURCE	pH	ALKALINITY	COLOUR	TURBIDITY	TOC
		mg/l	Hazen Units	FTU	mg/l
Belleville	7.2-8.5	87-117	40-50	0.9-6.0	8-14
Brantford	7.7-8.6	158-262	20-50	1.2-9.5	7-14
Cayuga	7.1-8.6	175-202	30-80	3.9-22	4-19
Humber R.	7.0-8.4	208-220	20-60	3.7-100	0-9

silica used in coagulation are 20.6 mg/l and 8.3 mg/l respectively. Average dosage of lime used is 19.7 mg/l.

2.3 Cayuga Water Treatment Plant

Cayuga Water Treatment Plant in the Town of Cayuga also receives its water from the Grand River.

The alkalinity, pH, colour and TOC of the raw water samples have normal variations during the study period (Table 1), except that the turbidity of the water may vary significantly after a rain storm.

The treatment process consists of pre-chlorination, coagulation with alum, sedimentation and dual-media filtration. The process schematic is shown in Figure 1. The plant is operated at $900 \text{ m}^3/\text{d}$ (0.24 MGD) serving a population of 1,200. The alum dose is 60 mg/l and the average chlorine dose is 6 mg/l with a free chlorine residual of 1 mg/l in the plant effluent.

2.4 The Ministry

Water from the Humber River is available at the Ministry's research area test facility and was also included in this study.

Some physical properties of the raw water vary with weather. For example, the turbidity of the raw water can be read up to 100 FtU after a rainfall; normally the turbidity is below 20 FtU. The water quality is shown in Table 1.

3. PROCEDURE

3.1 Jar Test Procedure

Coagulation investigations were conducted using jar-test techniques. The jar test system used in this study have five 1.5-litre square jars. The mixer used has impellers consisting of a one blade paddle. The diameter of the blade is 7.5 cm with projected area of 18.75 cm^2 . The mean velocity gradient, G at 100 rpm for this system is 140 s^{-1} (Appendix I). The dosages of all the chemicals used are given in Appendix II.

A series of jar tests, as listed in Table 2, was carried out at the laboratory of the Ministry with raw water samples collected at Belleville, Brantford, and Cayuga water treatment plants and shipped to the Ministry in 5 gallon glass bottles. The same series of tests was also repeated using Humber River water. All the jar tests were carried out at room temperature (20° C) and adjusted pH of 7.0 to 7.5. Jar tests #1 to #12 and #37 to #42 were repeated with duplicate samples from each water source while jar tests #13 to #36 were only carried out once.

The different sets of treatment conditions are as follows:

- 1) treatment using alum only as a coagulant
- 2) treatment using alum plus activated silica or a polyelectrolyte as a coagulant aid
- 3) treatment using alum and powdered activated carbon
- 4) treatment using alum plus activated silica or a polyelectrolyte and powdered activated carbon.
- 5) treatment using polyelectrolyte alone
- 6) pre-treatment with chlorine (before the usual jar test procedure)
- 7) pre-treatment with ozone
- 8) pre-treatment with potassium permanganate
- 9) pre-treatment with hydrogen peroxide

One litre of the water to be tested was placed in each jar and the pH of the water was adjusted to 7.0 to 7.5 with dilute sulfuric acid at room temperature of 20° C. The treatment chemicals were added while the contents were being stirred at 10.5 radians/sec (100 rpm) for five minutes. After this rapid stirring to ensure complete chemical dispersion, the stirring rate was decreased to 3.2 radians/sec. (30 rpm) and coagulation was allowed to continue for a period of 30 minutes. The stirring was then stopped and the floc was allowed to settle for 30 minutes. The supernatant was decanted and then analyzed for pH, turbidity and haloforms. The alum dosages were chosen adequately to bracket the usual alum dosages of the plant. As noted later that the optimum alum dosage was determined by turbidity.

TABLE 2

JAR TESTS

1. Raw + Alum + Cl₂
2. Raw + Cl₂ + Alum
3. Raw + 5 ppm PAC + Alum + Cl₂
4. Raw + 5 ppm PAC + Cl₂ + Alum
5. Raw + 20 ppm PAC + Alum + Cl₂
6. Raw + 20 ppm PAC + Cl₂ + Alum
7. Raw + Alum + Activated Silica + Cl₂
8. Raw + Cl₂ + Alum + Activated Silica
9. Raw + 5 ppm PAC + Alum + Activated Silica + Cl₂
10. Raw + 5 ppm PAC + Cl₂ + Alum + Activated Silica
11. Raw + 20 ppm PAC + Alum + Activated Silica + Cl₂
12. Raw + 20 ppm PAC + Cl₂ + Alum + Activated Silica
13. Raw + 570 C + Cl₂
14. Raw + Cl₂ + 570 C
15. Raw + Alum + 570 C + Cl₂
16. Raw + Cl₂ + Alum + 570 C
17. Raw + 5 ppm PAC + Alum + 570 C + Cl₂
18. Raw + 5 ppm PAC + Cl₂ + Alum + 570 C
19. Raw + 20 ppm PAC + Alum + 570 C + Cl₂
20. Raw + 20 ppm PAC + Cl₂ + Alum + 570 C
21. Raw + 847 A + Cl₂
22. Raw + Cl₂ + 847 A
23. Raw + Alum + 847 A + Cl₂
24. Raw + Cl₂ + Alum + 847 A

Con't..

25. Raw + 5 ppm PAC + Alum + 847 A + Cl₂
26. Raw + 5 ppm PAC + Cl₂ + Alum + 847 A
27. Raw + 20 ppm PAC + Alum + 847 A + Cl₂
28. Raw + 20 ppm PAC + Cl₂ + Alum + 847 A
29. Raw + 971 N + Cl₂
30. Raw + Cl₂ + 971 N
31. Raw + Alum + 971 N + Cl₂
32. Raw + Cl₂ + Alum + 971 N
33. Raw + 5 ppm PAC + Alum + 971 N + Cl₂
34. Raw + 5 ppm PAC + Cl₂ + Alum + 971 N
35. Raw + 20 ppm PAC + Alum + 971 N + Cl₂
36. Raw + 20 ppm PAC + Cl₂ + Alum + 971 N
37. Raw + O₃ + Alum + Cl₂
38. Raw + O₃ + Alum + Activated Silica + Cl₂
39. Raw + KMnO₄ + Alum + Cl₂
40. Raw + KMnO₄ + Alum + Activated Silica + Cl₂
41. Raw + H₂O₂ + Alum + Cl₂
42. Raw + H₂O₂ + Alum + Activated Silica + Cl₂

Note:

Raw	-	raw water
PAC	-	powdered activated carbon
570 C	-	Cationic polyelectrolyte
971 N	-	Nonionic "
847 A	-	Anionic "
Cl ₂	-	chlorine
O ₃	-	ozone
KMnO ₄	-	potassium permanganate
H ₂ O ₂	-	hydrogen peroxide
Alum dose	-	10, 20, 30, 40 & 50 mg/l
pH	-	7.0 to 7.5
Temperature	-	20° C
Cl ₂	-	to 1 mg/l free chlorine residual with 2 hours contact time

The coagulants used were alum, polyelectrolytes C (cationic), A (anionic) and N (nonionic), (Appendix II). These were used to determine whether coagulation using alum and these polyelectrolytes individually was effective in reducing the haloforms in the pre-chlorination tests and the haloform precursors in the post-chlorination tests. The effect of the addition of activated silica (Appendix II) and these polyelectrolytes as aids to alum coagulation was also studied.

3.2 Application of Chlorine

For the set of pre-chlorination tests in Table 2, chlorine solution (Appendix II) was added to the raw water to be tested, rapidly mixed for a minute and stored for an hour in the dark prior to coagulation and sedimentation. The chlorine dosage was determined to be the one which would give at least a 1 mg/l free chlorine residual after 2 hours contact time. The chlorinated raw water and the settled water after coagulation and sedimentation were sampled and dechlorinated with sodium thiosulfate solution (Appendix II). Samples of raw, chlorinated raw and chlorinated supernatant of the settled water were sent for haloform analysis.

For the set of post-chlorination tests in Table 2, chlorine solution was added to the supernatant drawn from the settled water after coagulation and sedimentation. The chlorinated supernatants were stored for two hours and then dechlorinated with sodium thiosulphate solution. As controls, samples of raw and chlorinated raw water were also sent for the haloform analysis with the chlorinated supernatants.

3.3 Pre-treatment with Alternate Disinfectants - Ozone, Potassium Permanganate and Hydrogen Peroxide

Water to be tested was first pre-treated with ozone or potassium permanganate or hydrogen peroxide (Appendix II). Jar tests were then carried out as in the post-chlorination test described in 3.2

Samples of raw, pre-treated raw, chlorinated raw, pre-treated and chlorinated raw, supernatant of settled water and chlorinated supernatant were sent for haloform analysis.

3.4 Adsorption by Activated Carbon

3.4.1 Powdered Activated Carbon (PAC)

Powdered activated carbon (PAC) (Appendix II) is often used for a taste and odour control; it is also effective in adsorbing general organics. PAC was therefore used in some of the jar tests to determine if there was any significant advantages to its use for reducing the haloforms and their precursors.

3.4.2 Granular Activated Carbon (GAC)

Adsorption of organics on granular activated carbon was studied by using the Carbon Adsorption Mini-Sampler (CAM Sampler)⁽¹⁴⁾ as shown in Figure 2.

The sampler is used by EPA in determining the organics in water by carbon adsorption. It is portable and easily set up at the test site.

Seventy grams of granular activated carbon, Filtrasorb 200, 14 x 40 mesh, were placed inside the filter. Raw water was pumped into the system, filtered by a micro-screen in the main tank (Figure 2) and then passed upward through the carbon filter at the rate of 20-22 ml/min., providing a contact time of about 4.5 minutes, for a 48-hour period. Once each 30 minutes, the carbon was flushed with raw water from the main tank in the same direction as sample flow for 7-8 seconds at a flow rate of about 400 ml/min, with a total flushing volume of 50-55 ml. The total volume of water passing through the activated carbon was measured by an electrode liquid level control system that collected one litre of volume and then drained and recorded the volume on a digital counter.

1. Main Tank - Constant Head
2. Main Tank Overflow Line
3. Influent to Main Tank
4. Sample Effluent from Main Tank
5. PVC Pipe - Main Tank Support
6. Feed Line Tee
7. Sample Column Feed Tank Valve
8. Sample Column Feed Tank
9. Sample Column Feed Tank Inlet
10. Sample Column Feed Tank Overflow Line
11. Flushing Valve
12. Sample Feed Water Line
13. Sample Column Flow Regulating Valve
14. Flushing Solenoid Valve
15. Sample Column Inlet Connection
16. Sample Column
17. Sample Column Outlet Tube
18. Sample Collector Funnel
19. Volume Measuring Tank
20. Volume Measuring Solenoid Valve
21. Volume Measuring Drain Cup
22. Influent Line - Swagelok Fitting
23. Power ON-OFF Switch
24. Volume Measurement Controller
25. Volume Digital Counter Recorder
26. Delay Timer - Set for 7-8 Seconds
27. 30-Minute Timer
28. Waste Drain
29. Top Fitting of Column
30. Electrical Connection for Volume Measurement
31. Influent Valve
32. Main tank support clips

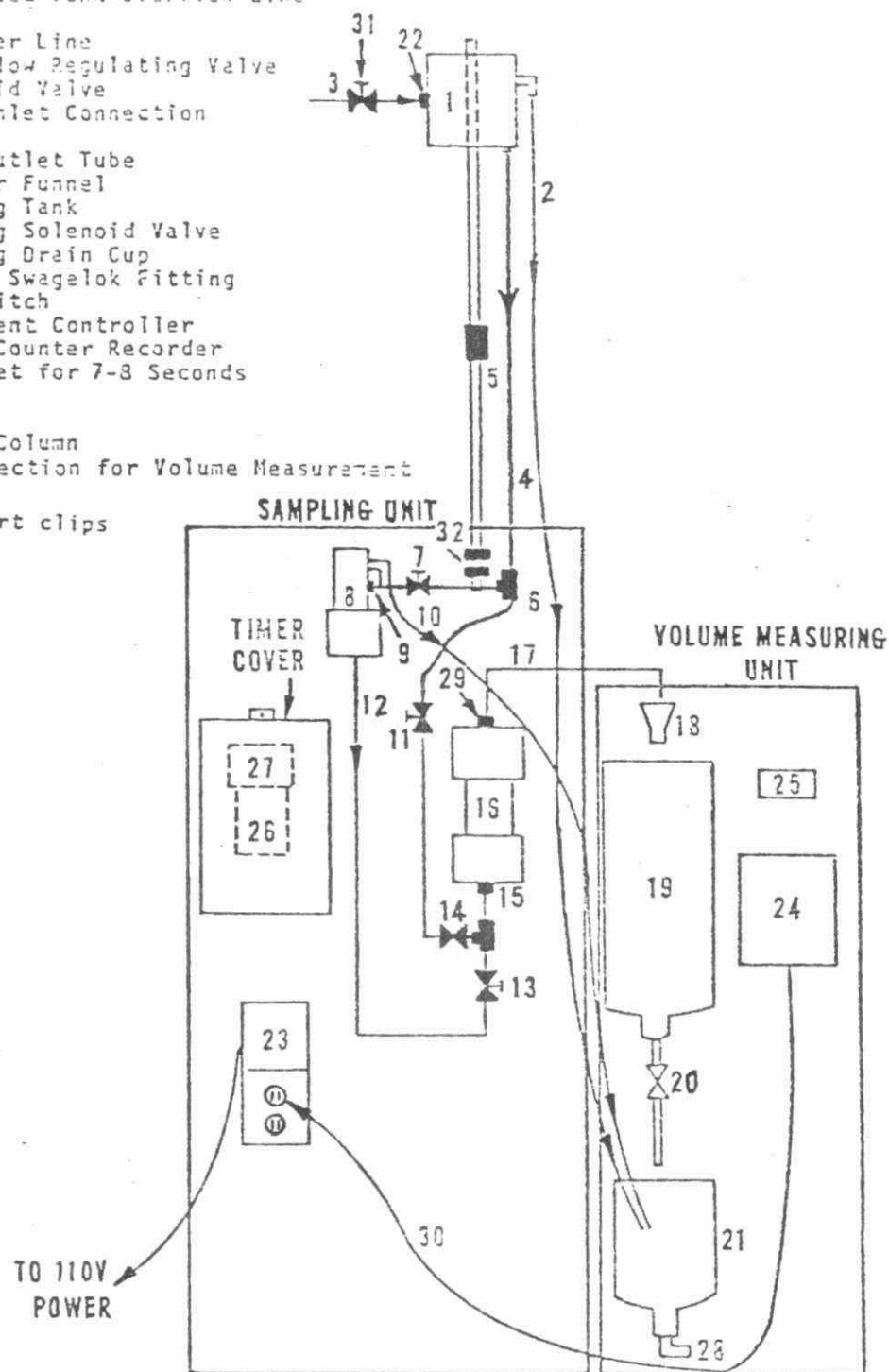


FIGURE 2 SCHEMATIC DIAGRAM OF MINI-SAMPLER

The CAM Sampler was first set up and operated in the laboratory for 2 days with distilled water passing through it to establish a system baseline or background. It was then set up at Belleville and Cayuga water treatment plants. Raw water was passed through the CAM Sampler continuously for 5 days. The carbon was removed and dried in an oven at 40⁰ C for 48 hours. The adsorbed materials were extracted with ethanol for 48-hours and a blank was run simultaneously.⁽¹⁵⁾ The ethanol extracts were then vacuum dried, evaporated to dryness and transferred to small vials. The extracted materials were weighed and redissolved in 10 mls. of methanol. The methanol solution was well mixed with distilled water which has been circulated through millipore filters (Appendix II) at the ratio of 1:4000 and 1:250 by volume. The solutions were chlorinated at 2 mg/l and 4 mg/l for samples from Belleville and Cayuga respectively. They were then analyzed for haloforms.

At the test sites, samples of the influent and effluent of the CAM Sampler were collected daily during the test period. They were brought back to the laboratory, chlorinated and then analyzed for haloforms.

4. RESULTS AND DISCUSSIONS

4.1 Coagulation

The optimum alum dosage was determined in each jar test by the best turbidity obtained. The corresponding results of the haloform analyses were then selected for further study.

4.1.1. Alum and Polyelectrolytes as Primary Coagulants

a) Alum

The results of the jar-tests using alum alone to remove haloform precursors are summarized in Table 3. They showed that alum coagulation was effective in reducing the haloform

TABLE 3 EFFECT OF ALUM COAGULATION WITH POST-
CHLORINATION ON CHLOROFORM FORMATION POTENTIAL

	Chloroform Concentration in ppb				% Reduction of of CHCl_3 format- ion potential	Average % Reduction of CHCl_3 formation potential
	Raw	Raw + Cl_2	Raw + Alum	Raw + Alum + Post- Cl_2		
Belleville						
7/12/76	4	134	ND	68	48	57
7/19/76	2	156	3	56	66	
6/21/77	1	102	ND	37	63	
6/27/77	ND	132	ND	46	65	
7/7/77	ND	82	ND	46	42	
Brantford						
7/26/76	11	138	14	91	39	42
7/26/76	6	99	18	57	57	
7/27/77	ND	86	ND	60	30	
Cayuga						
7/6/76	1	100	ND	64	35	40
6/1/77	ND	94	ND	58	38	
6/8/77	ND	82	ND	60	27	
7/12/77	ND	122	ND	55	55	
8/15/77	ND	136	ND	60	43	
Humber River						
5/20/76	ND	38	ND	34	11	31
5/17/77	ND	57	ND	41	28	
5/20/77	ND	59	ND	36	39	
5/25/77	ND	106	ND	60	44	

Temperature 20°C

pH-7.0 to 7.5

Cl_2 - 1 mg/L free chlorine residual with 2 hours contact time.

TABLE 4

SUMMARY OF THE PERCENTAGE REDUCTION OF
TOTAL POTENTIAL CHLOROFORM (PRE-CHLORINATION)
AND TOTAL FORMATION POTENTIAL OF CHLOROFORM
PRECURSORS (POST-CHLORINATION) BY COAGULATION/
SEDIMENTATION

WATER SOURCE	BELLEVILLE		BRANTFORD		CAYUGA		HUMBER RIVER	
Treatments Chemicals	pre-Cl ₂	post-Cl ₂	pre-Cl ₂	post-Cl ₂	pre-Cl ₂	post-Cl ₂	pre-Cl ₂	post-Cl ₂
Alum	16 50 37 *	48 66 63 65 42	16 * *	39 57 30	20 * 2 4	35 38 27 55	7 16 * * * *	11 28 39 44 33
Alum + 5 ppm PAC	17	5	24 5	24 * 49	40	47	9 16	26 29 53
Alum + 20 ppm PAC	NA	NA	35 53 39	42	40	66 39	50 *	47 24
Alum + 10% Activated Silica	28	86 88	60 32 *	85 87	24 *	98 98 99	22 11 *	99 89
Alum + 30% Activated Silica	13 24	87 91			13 15 19 *	90	* * 13 30 * 20 29 27 22 40	91 94 89 87 89 88 89 86 82 85
Alum + 5 ppm PAC + 10% A.S.	*	84 87	60 43 2	89 83	35	94 97	45 38 *	89 73
Alum + 20 ppm PAC + 10% A.S.	36	89 80	36 55	83 84	71	94	15 26	77
570 C	NA	NA	NA	NA	NA	NA	NA	NA
Alum + 570 C	*	64	43 24	36 10	*	39	62	62
Alum + 570C + 5 ppm PAC	52	53	* 69	9 56	14	52	NA	NA
Alum + 570 C + 20 ppm PAC	43	30	40	27	46	44	23	17

TABLE 4 (Con't)

WATER SOURCE	BELLEVILLE		BRANTFORD		CAYUGA		HUMBER RIVER	
Treatments Chemical	pre-Cl ₂	post-Cl ₂	pre-Cl ₂	post-Cl ₂	pre-Cl ₂	post-Cl ₂	pre-Cl ₂	post-Cl ₂
847A	NA	NA	NA	NA	NA	NA	*	25
Alum + 847 A	18	*	68	13	2	30	15	12
Alum + 847 A + 5 ppm PAC	55	56	42	0	8	7	20	54
Alum + 847 A + 20 ppm PAC	65	27	NA	NA	46	12	15	61
971N	NA	NA	NA	NA	NA	NA	10	45
Alum + 971 N	18	*	*	7	7	24	*	46
Alum + 971 N + 5 ppm PAC	NA	NA	30	0	34	63	19	41
Alum + 971 N + 20 ppm PAC	NA	NA	*	10	33	15	11	26

NA - not available

* - negative reduction

TABLE 5 EFFECT OF CHANGING THE POINT OF
CHLORINE APPLICATION ON PERCENTAGE REDUCTION
OF CHLOROFORM AND CHLOROFORM PRECURSORS.

Coagulants and Aids	AVERAGE PERCENTAGE REDUCTION OF			
	CHLOROFORM		CHLOROFORM PRECURSORS	
		(*)		(*)
Alum	20	(10)	42	(17)
Alum + 5 mg/L PAC	19	(6)	33	(7)
Alum + 20 mg/L PAC	43	(5)	44	(5)
Alum + 10% Activated Silica	30	(6)	92	(9)
Alum + 30% Activated Silica	22	(12)	88	(13)
Alum + 5 mg/L PAC + 10% Activated Silica	37	(6)	87	(8)
Alum + 20 mg/L PAC + 10% Activated Silica	40	(6)	85	(6)
Alum + 570 C	43	(3)	42	(5)
Alum + 570 C + 5 mg/L PAC	45	(3)	43	(4)
Alum + 570 C + 20 mg/L PAC	38	(4)	30	(4)
Alum + 847A	26	(4)	18	(3)
Alum + 847A + 5 mg/L PAC	31	(4)	39	(4)
Alum + 847A + 20 mg/L PAC	42	(3)	33	(3)
Alum + 971N	13	(2)	26	(3)
Alum + 971N + 5 mg/L PAC	28	(3)	52	(3)
Alum + 971N + 20 mg/L PAC	22	(2)	17	(3)

TABLE 5 is also a summary of the average percentage reduction of chloroform and chloroform precursors.

(*) Number of samples

precursors before chlorination. It was found that as high as 66% reduction of chloroform formation potential was obtained in the water tested (Table 3). Water samples from Belleville, Brantford, Cayuga and Humber River had respectively an average of 57%, 42%, 40% and 31% reductions of chloroform formation potential (Table 3). A reduction of 42% of chloroform formation potential was the overall average resulting from alum coagulation and post-chlorination (Table 5). The percentage reduction of chloroform formation seemed to be unrelated to the initial concentration of the chloroform precursors. For example, 134 $\mu\text{g/l}$ and 82 $\mu\text{g/l}$ of chloroform were obtained in the two chlorinated raw water samples from Belleville (Table 3) and 68 $\mu\text{g/l}$ and 46 $\mu\text{g/l}$ of chloroform were obtained in the settled water upon chlorination, leading to similar percentage reductions of chloroform formation potential of 48% and 42%.

b) Polyelectrolytes

The results of the jar tests using polyelectrolytes are summarized in Table 4. Polyelectrolytes C and A failed to give settleable floc with all the water tested (Table 4) when they were used as sole coagulants. The increase of their dosages or the adjustments of the pH of the water did not help to improve the formation of floc. Polyelectrolyte N was able to produce satisfactory floc with Humber River water, but formation of floc with Belleville, Brantford and Cayuga water was not successful. The preliminary results obtained demonstrated that coagulation using these polyelectrolytes with Belleville, Brantford, Cayuga and Humber River water was so poor that jar testing using these

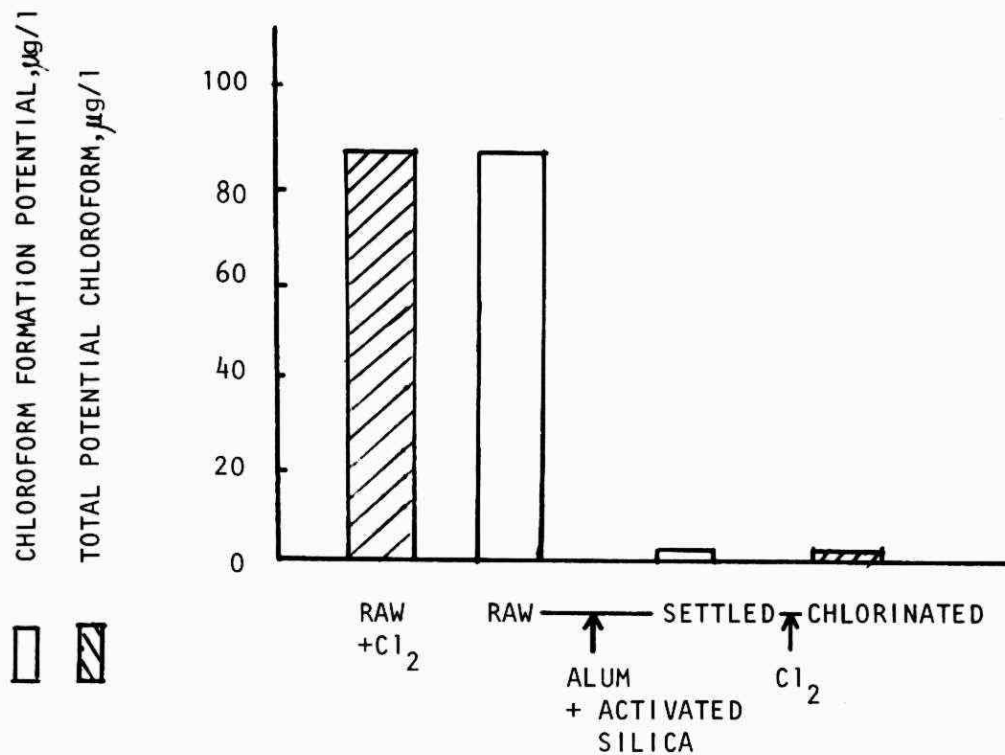


FIGURE 3 REDUCTION OF CHLOROFORM PRECURSORS IN CAYUGA WATER USING ALUM, ACTIVATED SILICA AND POST-CHLORINATION

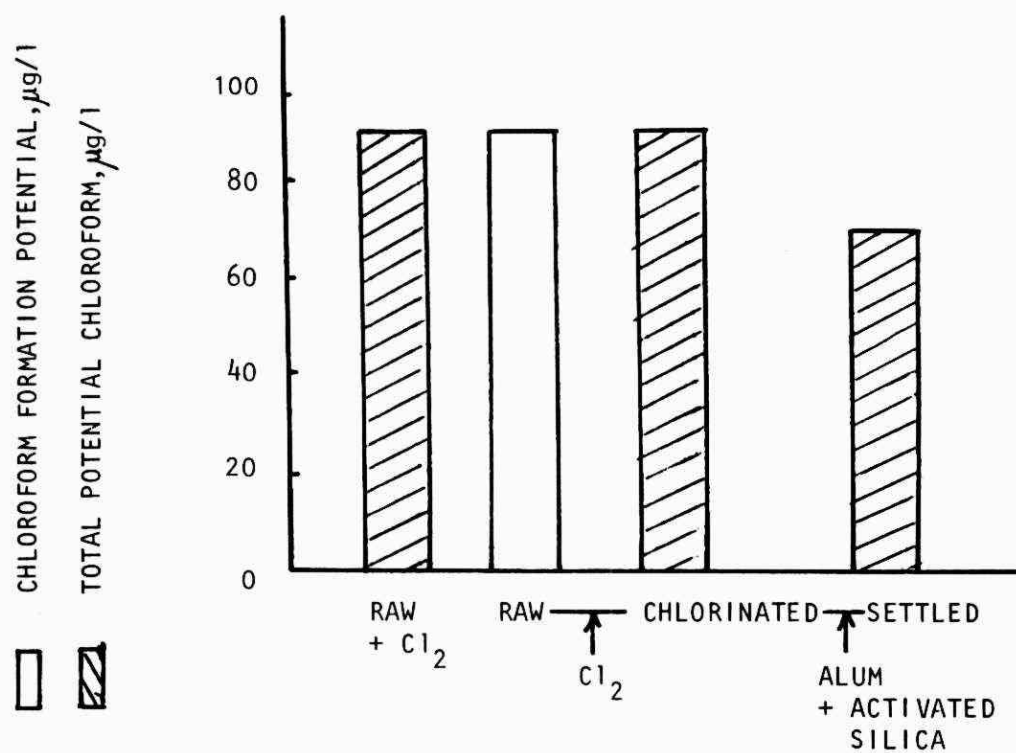


FIGURE 4 REDUCTION OF CHLOROFORM IN CAYUGA WATER USING ALUM, ACTIVATED SILICA AND PRE-CHLORINATION

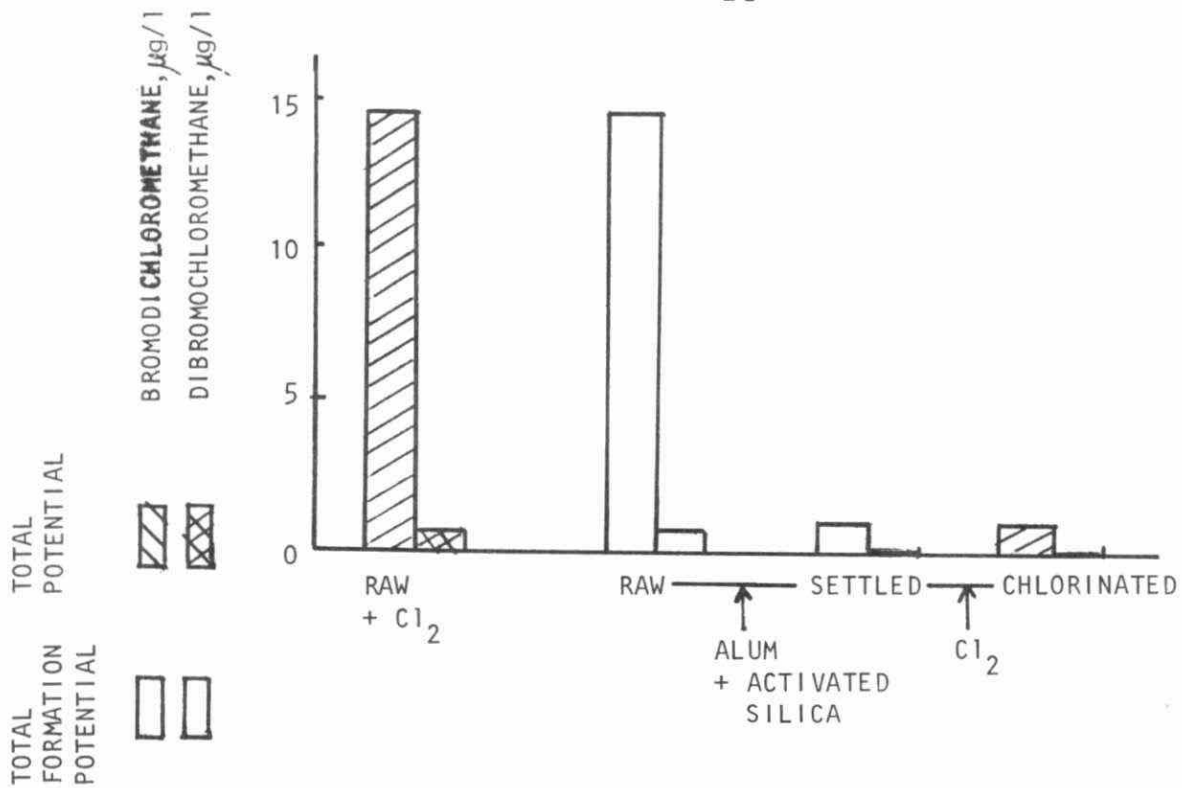


FIGURE 5 REDUCTION OF BROMODICHLOROMETHANE AND DIBROMOCHLOROMETHANE PRECURSORS IN CAYUGA WATER USING ALUM, ACTIVATED SILICA AND POST-CHLORINATION

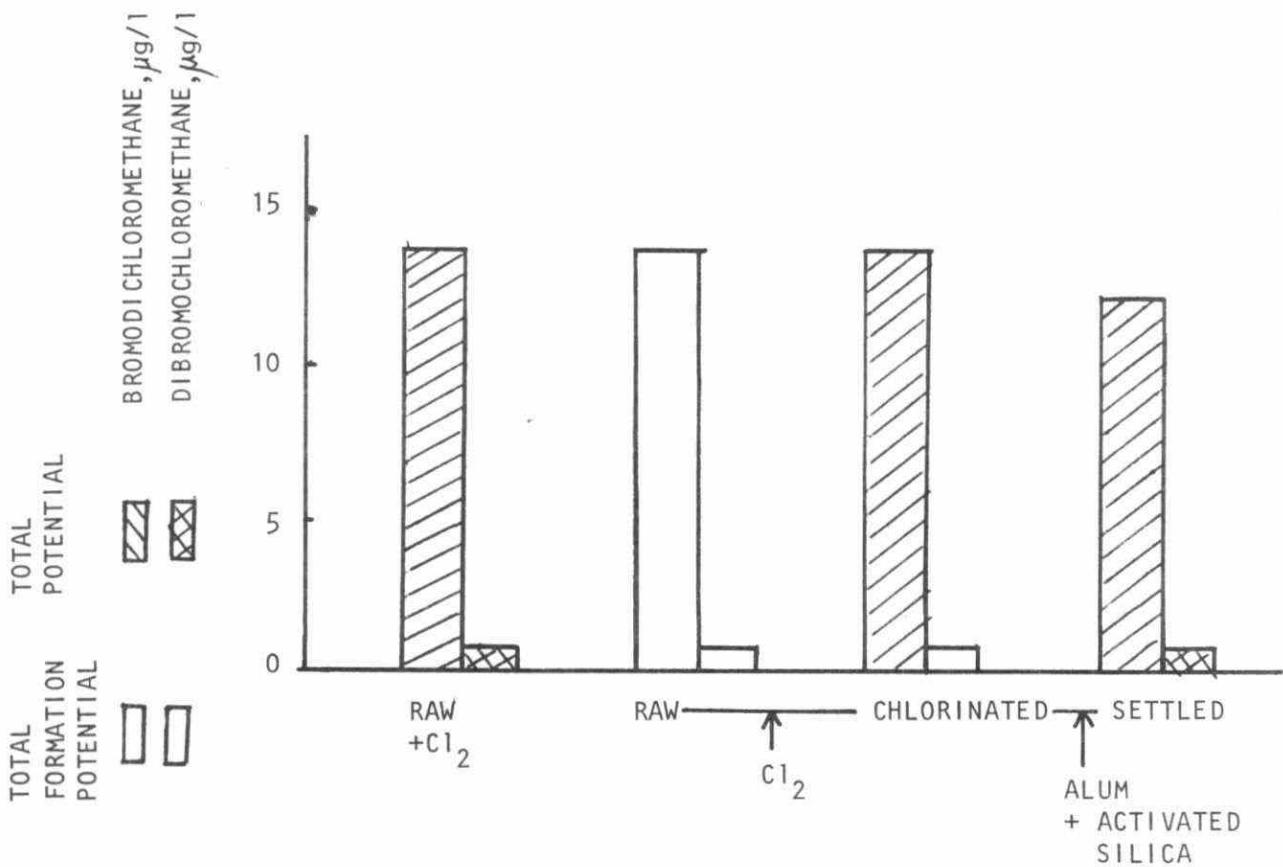


FIGURE 6 REDUCTION OF BROMODICHLOROMETHANE AND DIBROMOCHLOROMETHANE IN CAYUGA WATER USING ALUM, ACTIVATED SILICA AND PRE-CHLORINATION

polyelectrolytes as primary coagulants were discontinued.

4.1.2 Alum with Coagulant Aids

a) Activated Silica

The results from treatment with alum and activated silica for the removal of haloform precursors are summarized in Table 6. Activated silica has indicated a greater potential for reducing chloroform precursors than cationic, anionic and nonionic polyelectrolytes used as aids to alum coagulation (Table 4).

An average of 92% reduction of chloroform formation potential was obtained from alum coagulation with activated silica and post-chlorination while only 42%, 18% and 26% reductions were obtained from alum coagulation with polyelectrolytes C, A or N respectively and post-chlorination (Table 5).

Data on alum coagulation with activated silica are illustrated in the form of bar graphs and represent the effective treatment conditions for minimizing the concentration of chloroform and other haloforms in the tested water (Figures 3 & 5). In the case of the raw water that was chlorinated, stored for two hours and dechlorinated, the values of the chloroform represented the maximum concentration of chloroform that could be expected or the formation potential of the chloroform precursors in the raw water. In the case of the coagulated/settled water that was post-chlorinated, stored for two hours and dechlorinated, the values of chloroform represented the maximum chloroform concentration that could be expected in the coagulated/settled

water, and indicated the change in formation potential of the chloroform precursors as a result of the coagulation/sedimentation. In the case of water that was pre-dechlorinated, coagulated and settled, the values of chloroform represented the maximum concentration of the chloroform remaining in the settled water after coagulation/sedimentation, and indicated the reduction of chloroform by coagulation/sedimentation after it was formed.

Levels of 82 $\mu\text{g/l}$ of chloroform, 14 $\mu\text{g/l}$ of dibromochloromethane and 1 $\mu\text{g/l}$ of dibromochloromethane were found in the chlorinated raw water of Cayuga (Figures 3 & 5), and only 2 $\mu\text{g/l}$ of chloroform, 1 $\mu\text{g/l}$ of bromodichloromethane and 1 $\mu\text{g/l}$ of dibromochloromethane were obtained in the coagulated/settled water. This accounted for 98%, 93% and over 99% reductions of the formation potential of chloroform, bromodichloromethane and dibromochloromethane respectively by alum coagulation with activated silica and post-chlorination. Similar favourable results were also obtained from the same mode of operation on Belleville, Brantford and Humber River. The results are shown in Table 6. An average of 88%, 87%, 96% and 89% reductions of chloroform formation potential were obtained from Belleville, Brantford, Cayuga and Humber River water respectively giving an overall average of 92% reduction (Table 5). The percentage reductions of the individual municipal water were found to be more or less the same regardless of the initial levels of the chloroform precursors in the raw water. There were 146 $\mu\text{g/l}$ and 62 $\mu\text{g/l}$ chloroform in the two chlorinated raw water samples from Humber River and as a result of alum and activated silica coagulation, there were 16 $\mu\text{g/l}$

TABLE 6
EFFECT OF ALUM COAGULATION WITH ACTIVATED
SILICA AND POST-CHLORINATION ON CHLOROFORM
FORMATION POTENTIAL

	Chloroform Concentration in ppb				% Reduct- ion of CHCl ₃ formn. potential	Average % Reduction of CHCl ₃ formn. potential
	Raw	Raw+ Cl ₂	Raw + Alum + A.S.	Raw + Alum + A.S.+ post-Cl ₂		
Belleville						
7/20/76	4	124	1	18	86	88
10/1/76	3	84	3	13	88	
6/22/77	3	130	ND	17	87	
6/29/77	2	127	ND	11	91	
Brantford						
10/5/76	ND	60	ND	9	85	87
7/21/77	ND	130	ND	4	89	
Cayuga						
6/22/76	ND	44	6	7	98	96
7/12/76	ND	82	ND	2	98	
8/23/76	ND	29	ND	ND	99+	
6/9/77	1	89	ND	10	90	
Humber River						
6/3/76	3	95	ND	1	99	89
9/1/76	7	62	ND	6	89	
5/3/77	ND	76	ND	7	91	
5/6/77	ND	67	ND	4	94	
5/19/77	ND	78	ND	9	89	
5/24/77	ND	69	ND	9	87	
5/27/77	ND	146	ND	16	89	
5/30/77	ND	140	ND	16	89	
6/14/77	ND	65	ND	9	86	
6/13/77	ND	60	ND	11	82	
6/16/77	ND	75	ND	11	85	

CHCl₃ - Chloroform

A.S. - Activated Silica

and 6 $\mu\text{g}/\text{l}$ of chloroform in the respective samples of the settled water upon chlorination. In both cases 89% reduction of chloroform formation potential was obtained.

Comparing the percentage reductions of chloroform formation potential by alum coagulation with post-chlorination and those by alum coagulation with activated silica and post-chlorination (Tables 3 & 6), it showed that the addition of activated silica as an aid to alum coagulation increased the percentage reduction of chloroform formation potential from 42% to 92%.

It was also found that the effectiveness in reducing chloroform formation potential was almost unchanged by any increase of activated silica dose. When the dosage of activated silica was increased from 10% to 30% of the corresponding alum dosage, an overall average of 88% reduction of chloroform formation potential was obtained (Table 5). Therefore it was considered that any increase in activated silica dose was insignificant in terms of reduction of chloroform formation potential. Larger floc and better settling rates were observed however with the higher dosage of activated silica. It was therefore concluded that the increase in the dosage of activated silica did not further improve the reduction of chloroform formation potential, but improved the performance of coagulation.

The conclusion was reached that the treatment condition using alum, activated silica and post-chlorination was one of the best treatment modes of operation for minimizing the formation of chloroform in the treated water.

b) Polyelectrolytes

The overall performance of polyelectrolytes C, A and N as aids to alum was poor in this study. The floc formed was usually so fine and scarce that long settling times were required. There were also some inconsistencies in their performance pertaining to the reduction of haloforms. More consistent removal of haloforms might occur if filtration had been a part of the treatment train. In some cases, higher percentage removals of haloforms were obtained with pre-chlorination compared with post-chlorination treatments. For example, 68% reduction was obtained from alum coagulation with polyelectrolyte A and pre-chlorination on Brantford water while only 13% reduction was found with the same mode of treatment operation except with post-chlorination (Table 4). This is contradictory to the other results which have indicated that it was more effective to remove chloroform precursors than chloroform after it is formed. The significance of the point of chlorination will be discussed later in Section 4.3

In another case, the same reduction of 62% was obtained from pre-chlorination compared with post-chlorination using alum coagulation and polyelectrolyte C (Table 4). In other cases, higher percentage reductions were observed when post-chlorination was used rather than pre-chlorination. This agreed with the results discussed in Section 4.1.1. For example, 30% and 2% reductions of chloroform formation potential were obtained from post-chlorination and pre-chlorination respectively with alum coagulation and polyelectrolyte A on Cayuga water (Table 4).

TABLE 7

EFFECT OF
ALUM COAGULATION WITH ACTIVATED
SILICA AND PRE-OZONATION ON REDUCTION
OF CHLOROFORM FORMATION POTENTIAL

	Raw	Raw + Cl ₂	Raw + O ₃	Raw + O ₃ + Cl ₂	Raw + O ₃ + Alum + activated silica	Raw + O ₃ + Alum + activated silica + post-Cl ₂	% Reduction of chloroform formation potential by O ₃ alone	Overall % Reduction of Chloroform Formation Potential
Belleville								
7/14/77	ND	100	ND	99	ND	14	1	86 (86)
Brantford								
7/22/77	ND	124	ND	110	ND	7	11	94 (78)
7/28/77	ND	142	ND	39	ND	55	73	61
Cayuga								
6/9/77	1	85	2	80	1	9	7	89 (90)
6/3/77	2	200	ND	92	ND	4	54	98
6/2/77	ND	111	ND	97	ND	19	13	83
Humber River								
5/27/77	ND	153	ND	108	ND	14	29	91 (91)

Total Potential Chloroform in ppb

TABLE 8 SUMMARY OF THE PERCENTAGE REDUCTION OF CHLOROFORM
AND CHLOROFORM PRECURSORS BY COAGULATION/SEDIMENTATION
WITH PRE-TREATMENT OF CHLORINE, OZONE, POTASSIUM
PERMANGANATE OR HYDROGEN PEROXIDE

WATER SOURCE	BELLEVILLE		BRANTFORD		CAYUGA		HUMBER RIVER	
Chemicals Treatment	Alum	Alum + Activated Silica	Alum	Alum + Activated Silica	Alum	Alum + Activated Silica	Alum	Alum + Activated Silica
Pre-ozonation/ post- chlorination	67 69	86	42 34	61 94	40 36	89 98 83	46	91
Pre-chlorination	50 37 15	13 24 20	8 56 26	20	4 2 23	13 15 19 26	23	20 27 29 22 40
Post-chlorination	63 65 42	87 91 73	30	89	27 28 55	90 75 91	44	86 82 85 89 88
Pre-treatment with KMnO ₄ /post- chlorination	59 58 73	83 86 92	73 40	83	58 50	94		48 41 76 77 84
Pre-treatment with H ₂ O ₂ /post- chlorination	47 74 60	89 97 93	45 86	94 91	74 91	88		96

The reasons for the inconsistencies in the performance of these polyelectrolytes as aids in alum coagulation are not known. However, the results indicate that they gave little or no aid in coagulation. The series of tests using the polyelectrolytes were then discontinued in this study.

4.2 Pre-treatment with Other Disinfectants

4.2.1 Ozone

The results of coagulation with pre-ozonation are summarized in Table 7. The concentration of chloroform was found to be higher in the chlorinated raw water than in the ozonated raw water upon chlorination. The data indicate that there was a decrease in chloroform formation following ozonation of raw water. It is possible that some of the chloroform precursors were oxidized by ozone to other organic compounds which later did not produce chloroform upon chlorination. Rook ⁽³⁾ reported that ozonation of natural waters prior to chlorination would reduce chloroform production by 50% provided that chlorination followed shortly after ozonation. However, Lawrence ⁽¹⁶⁾ and Riley ⁽¹⁷⁾ have shown that ozonation may actually increase the amount of haloforms formed after chlorination. Love, Miltner and Symons ⁽⁹⁾ also showed that ozonation/chlorination treatment of drinking water may enhance chloroform production. The decrease in chloroform production in the ozonated raw water was in the range of 1% to 73% for water from Belleville, Brantford, Cayuga and the Humber River (Table 7). An average of 31% reduction in chloroform formation was obtained by pre-treatment with ozone alone.

TABLE 9

EFFECT OF ALUM COAGULATION WITH ACTIVATED SILICA
AND PRE-TREATMENT WITH POTASSIUM PERMANGANATE
ON REDUCTION OF CHLOROFORM FORMATION POTENTIAL

	Raw	Raw + Cl ₂	Raw + KMnO ₄	Raw + KMnO ₄ + Cl ₂	Raw + KMnO ₄ + Alum + Activated Silica	Raw + KMnO ₄ + Alum + Activated Silica + post-Cl ₂	% Reduct- ion of chloroform formation potential by KMnO ₄ alone	Overall % Reduction of Chloroform Formation Potential	
Belleville									
6/23/77	1	119	ND	127	ND	21	-6	83	
6/30/77	ND	96	ND	127	ND	9	-16	92	(87)
7/8/77	ND	50	ND	137	ND	19	-64	86	
Brantford									
7/26/77	ND	54	ND	127	ND	22	-57	83	(83)
Cayuga									
7/13/77	ND	88	ND	106	ND	6	-17	94	(94)
Humber River									
6/7/77	1	82	2	72	ND	20	12	76	
6/13/77	1	60	ND	71	ND	14	-15	77	(79)
6/14/77	ND	63	ND	63	ND	10	0	84	
Total Potential Chloroform in ppb									

The overall percentage reductions of chloroform formation potential by ozonation and coagulation/sedimentation are summarized in Table 8. The average of the overall percentage reductions of 48% and 86% were obtained for treatments using alum only and alum with activated silica (Table 11). A portion of the values given above was possibly due to the oxidation of chloroform precursors whilst the remainder would be due to the effect of coagulation/sedimentation.

It was found that the quality of floc was changed in tests using pre-treatment of ozone. The floc formed was finer and denser than that with pre-chlorination or without pre-treatment at all. The turbidity of the settled water, however, was unaffected.

From the results obtained, it appears that it would be feasible to replace chlorine with ozone in the pre-treatment process in Belleville, Brantford and Cayuga water treatment plants in order to minimize the formation of chloroform in the treated water as well as provide effective control of taste and odour. However, careful study on ozone by-products is necessary.

4.2.2 Potassium Permanganate

After pre-treatment with potassium permanganate, there was usually an increase in chloroform formation upon chlorination in the raw water from Belleville, Brantford and Cayuga.

The concentrations of chloroform before and after treatment with potassium permanganate were shown in Table 9. An increase of 6% to 64% or an average of 21% increase in chloroform formation potential were obtained in the pre-

treatment water from Belleville, Brantford and Cayuga. This suggests that some of the organics in the tested water were oxidized by potassium permanganate to haloform precursors, resulting in a higher concentration of haloforms precursors in the raw water before coagulation and sedimentation. Therefore, a higher concentration of chloroform would be obtained upon chlorination.

However, there was an increase, a zero increase and a decrease of the chloroform formation potential in the raw water from the Humber River upon chlorination after the pre-treatment with potassium permanganate. The reasons may be due to the oxidation-reduction reactions of the permanganate ions in aqueous solutions under different reaction conditions. potassium permanganate.

As indicated previously, (page 14) alum coagulation was generally capable of reducing the chloroform formation potential by 42%, pre-treatment with potassium permanganate however helped to improve the average reduction to 64% (Table 11).

Improvements in the reduction of chloroform levels were observed in cases of Belleville, Brantford and Cayuga water, while there was no indication of improvement in the case of the Humber River water.

No improvements of chloroform formation potential occurred using alum coagulation with activated silica and pre-treatment with potassium permanganate compared with using no potassium

TABLE 10

ALUM COAGULATION WITH ACTIVATED
SILICA AND PRE-TREATMENT WITH
HYDROGEN PEROXIDE

	Raw	Raw + Cl ₂	Raw + H ₂ O ₂ +	Raw + H ₂ O ₂ + Cl ₂	Raw + H ₂ O ₂ + Alum + Activated Silica	Raw + H ₂ O ₂ + Alum + Activated Silica + post-Cl ₂	% Reduct- ion of CHCl ₃ formation potential by H ₂ O ₂ only	Overall % Reduction of CHCl ₃ format- ion potential
Belleville								
6/24/77	1	120	1	68	ND	13	44	89
6/29/77	ND	144	ND	31	ND	4	78	97
7/8/77	ND	131	ND	11	ND	9	92	93
Brantford								
7/21/77	ND	125	ND	27	ND	11	78	91
7/29/77	ND	124	ND	20	ND	7	84	94
Cayuga								
7/15/77	ND	124	ND	49	ND	15	60	88
Humber River								
6/17/77	1	72	1	15	ND	4	80	96
Total Potential Chloroform in ppb								

permanganate. An average of 87%, 83% and 94% reductions of chloroform formation were obtained in Belleville, Brantford and Cayuga water respectively, whereas 79% reduction was obtained in Humber River water. (Table 9)

The turbidities of the settled water in the tests with potassium permanganate treatment were noticeably higher than those without permanganate, and in many cases the settled water was slightly yellow in colour. This was probably due to manganese dioxide, MnO_2 , which should be easily removed by filtration.

The disadvantage of using potassium permanganate as an alternate disinfectant in pre-treatment process is that its application at water plants is usually found to be difficult to control. Improper application may result in pink or yellowish product water. The bacteriological quality of the treated water has to be examined and evaluated in addition to its effectiveness in haloform reduction.

4.2.3 Hydrogen Peroxide

Reductions of 78% and 93% of chloroform production were obtained in treatment with hydrogen peroxide using alum and alum plus activated silica respectively (Table 11). Alum coagulation with activated silica and pre-treatment with hydrogen peroxide was found to be one of the most effective treatment conditions which gave the highest percentage reduction of chloroform formation potential among all the treatment conditions tested. Good floc quality and short settling times were obtained in the tests with Belleville, Brantford, Cayuga and Humber River water. Comparing the levels of chloroform in the chlorinated raw water with pre-treatment of hydrogen peroxide and that without pre-treatment of hydrogen

TABLE 11 AVERAGE PERCENTAGE REDUCTION
OF CHLOROFORM PRECURSORS WITH
AND WITHOUT PRE-TREATMENT OF
ALTERNATE DISINFECTANTS

AVERAGE PERCENTAGE REDUCTION OF CHLOROFORM PRECURSORS			
COAGULANTS AND AIDS	with pre-treatment of		
	Ozone	Potassium Permanganate	Hydrogen Peroxide
Alum	48	64	78
Alum + 10% Activated Silica	86	76	93
	with no pre-treatment		
Alum	42		
Alum + 10% Activated Silica	92		

peroxide, it was found that hydrogen peroxide itself effected an average of 70% reduction of chloroform precursors (Table 10). This might indicate that hydrogen peroxide was capable of oxidizing most of the precursors to other compounds, thus resulting in a lower chloroform concentration following chlorination.

Hydrogen peroxide pre-treatment appears to cause a greater reduction of chloroform precursors than that caused by alum coagulation with activated silica.

4.2.4 General Disucussion on Alternate Disinfectants

Potassium permanganate and hydrogen peroxide have not been used as disinfectants in water treatment and generally they are used in taste and odour control. In this study, ozone did not alter the performance of subsequent alum coagulation with or without activated silica in the reduction of chloroform precursors. Potassium permanganate altered the effectiveness of chloroform precursor removal slightly in the subsequent coagulation and sedimentation treatment and hydrogen peroxide significantly affected the removal of chloroform precursors by alum coagulation (without activated silica) and did not alter the performance of alum coagulation when activated silica was used. However, the by-products of these alternate disinfectants are essentially unknown. In order to ensure treated water free of hazards, the alternate disinfectant should be effective as a disinfectant as well as minimizing the formation of chloroform and at the same time not producing toxic or potentially toxic by-products.

4.3 Changing the Point of Chlorine Application

Changing the point of chlorine application resulted in a change of chloroform concentration in the treated water. Data obtained operating with pre-chlorination and post-chlorination have been compared for every coagulant and coagulant aid used.

The average percentage reduction of chloroform in the treated water with different coagulation conditions is shown in Table 2. It was found that higher chloroform concentrations were obtained in treated water with pre-chlorination than with post-chlorination under the following coagulation conditions:-

- 1) using alum only
- 2) using alum and activated silica
- 3) using alum and PAC
- 4) using alum, activated silica and PAC

In each mode of operation, higher percentage reductions of chloroform precursors or lower levels of chloroform in the treated water were usually obtained with post-chlorination compared with pre-chlorination and the data are shown in Table 5. It was found that the percentage reductions were increased by 100% to 150% if chlorine was applied after coagulation/sedimentation. Figures 3 and 4 illustrate the significant improvement in reducing the chloroform production by post-chlorination. Treatment of Cayuga water produced a 24% reduction of chloroform with alum, activated silica and pre-chlorination, while 98% reduction of chloroform formation potential was obtained from the same treatment but this post-chlorination.

Data developed during this study have also demonstrated similar favourable results on the production of bromodichloromethane and

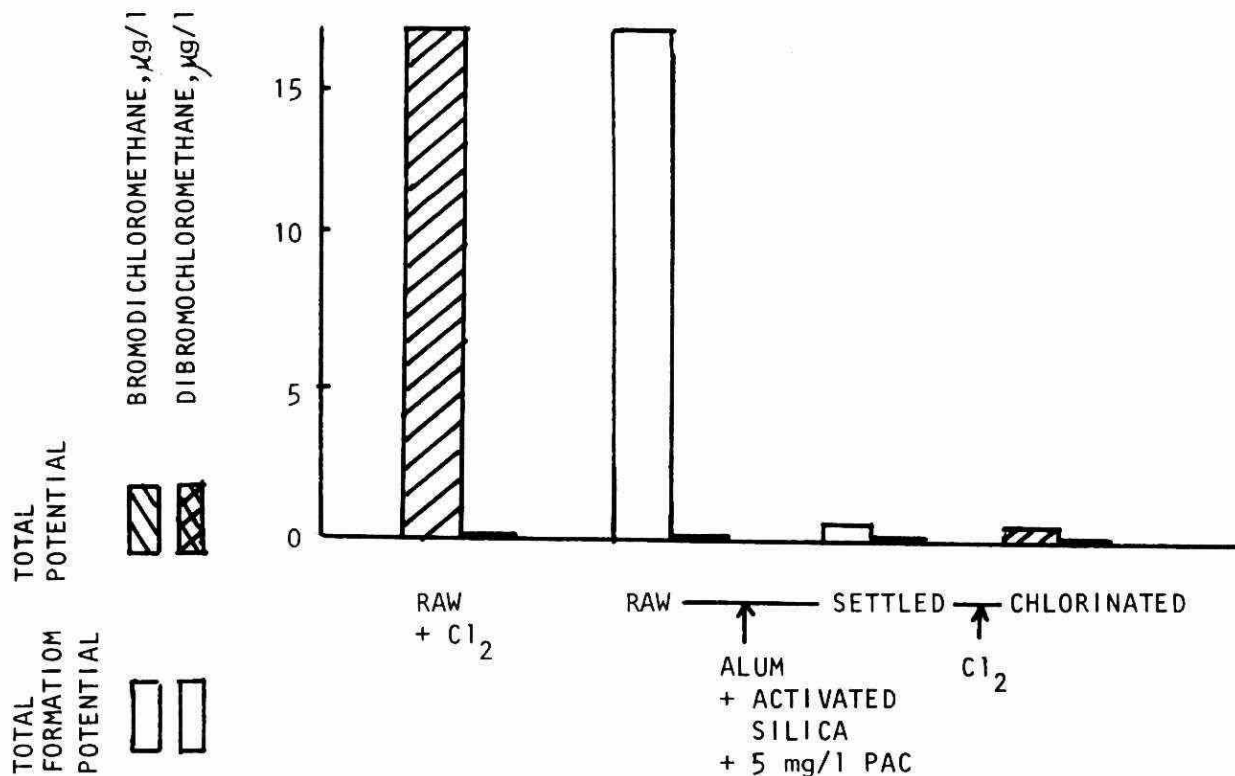


FIGURE 7 REDUCTION OF BROMODICHLOROMETHANE AND DIBROMOCHLOROMETHANE PRECURSORS IN CAYUGA WATER USING ALUM, ACTIVATED SILICA, 5 ppm PAC AND POST-CHLORINATION

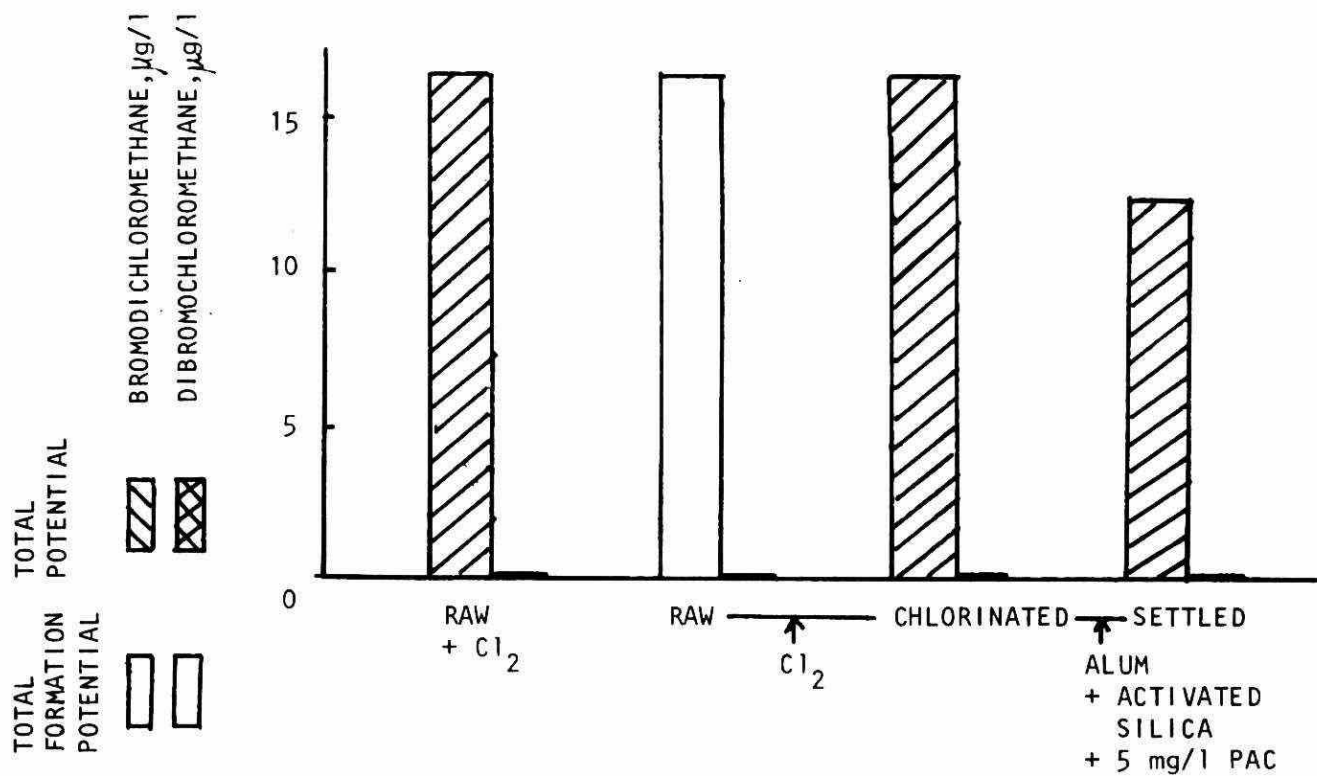


FIGURE 8 REDUCTION OF BROMODICHLOROMETHANE AND DIBROMOCHLOROMETHANE IN CAYUGA WATER USING ALUM, ACTIVATED SILICA, 5 ppm PAC AND PRE-CHLORINATION

dibromochloromethane. Over 99% reduction of their formation potential was obtained with post-chlorination treatment while less than 30% removal was obtained following pre-chlorination. The difference is illustrated in Figure 5 and 6 using alum and activated silica coagulation, and in Figures 7 and 8, using alum and activated silica plus 20 mg/l PAC.

The effect of moving the point of chlorination to follow coagulation/sedimentation was obscure when treatment chemicals other than alum alone or with activated silica and PAC were used. Treatments using alum and polyelectrolytes C, A or N with or without the addition of PAC, indicated a similar percentage reduction of chloroform in pre-chlorination tests and chloroform precursors in post-chlorination tests. It was found that in some cases the percentage removals of chloroform was even higher with pre-chlorination tests. The reason for this is not clear, but it could have been caused by the failure of the chloroform precursors to complex with alum and the polyelectrolyte; these erratic results of polyelectrolyte have been discussed before.

These data indicate that coagulation with alum and activated silica was effective in reducing the chloroform precursors before chlorination and later resulted in a lower chloroform concentration upon chlorination. It was also shown that coagulation with pre-chlorination was not very effective in removing chloroform after it was formed. Therefore, minimum chloroform concentrations could be obtained when chlorination was applied after coagulation and sedimentation.

4.4 Adsorption

4.4.1 Powdered Activated Carbon (PAC)

The effectiveness of PAC for reducing the levels of chloroform precursors prior to chlorination and of chloroform after it was formed, is indicated by the results summarized in Tables 4 & 5. There were no significant improvements in reducing the chloroform precursors or chloroform itself with the addition of PAC. There were only slight increases in the percentage reductions of chloroform and its formation potential when the PAC dose was increased from 5 mg/l to 20 mg/l in coagulation using alum only. The average percentage reduction of chloroform was increased from 19% to 43% while the average percentage reduction of chloroform precursors was increased from 33% to 45%.

Positive and negative reductions were obtained with the increase of PAC dosages in coagulation using polyelectrolytes C, A or N. For example, alum coagulation with anionic polyelectrolyte (PEA) on Humber River water resulted in 15% and 12% removals for pre-chlorination and post-chlorination respectively; whereas under the same treatment conditions but with the addition of 5 mg/l PAC, 20% and 54% removals were obtained with pre-chlorination and post-chlorination respectively (Table 4). In another case when 5 mg/l PAC were used with alum and PEA in the coagulation test on Belleville water, 55% and 56% reduction of chloroform and its precursors were obtained from pre-chlorination and post-chlorination respectively. However, when the dosage of PAC was increased to 20 mg/l, 65% and 27% reductions were obtained from pre-chlorination and post-chlorination respectively (Table 4).

FIGURE 9 ADSORPTION ON GRANULAR ACTIVATED CARBON
FOR ~~REDUCING~~ CHLOROFORM PRECURSORS
IN CAYUGA WATER MAY, 1976

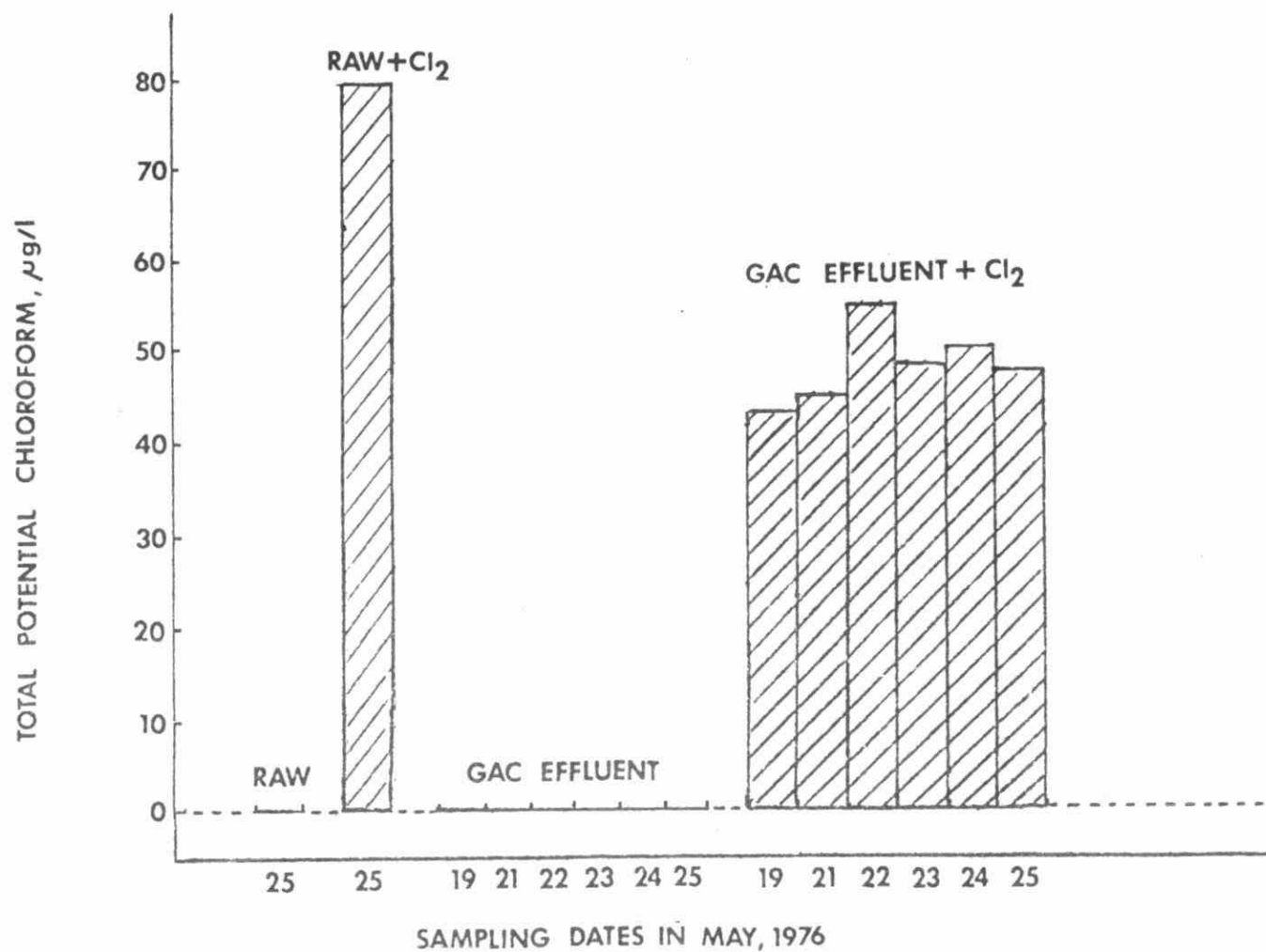


FIGURE 10 ADSORPTION ON GRANULAR ACTIVATED CARBON
FOR REDUCING CHLOROFORM PRECURSORS
IN BELLEVILLE WATER JULY, 1976

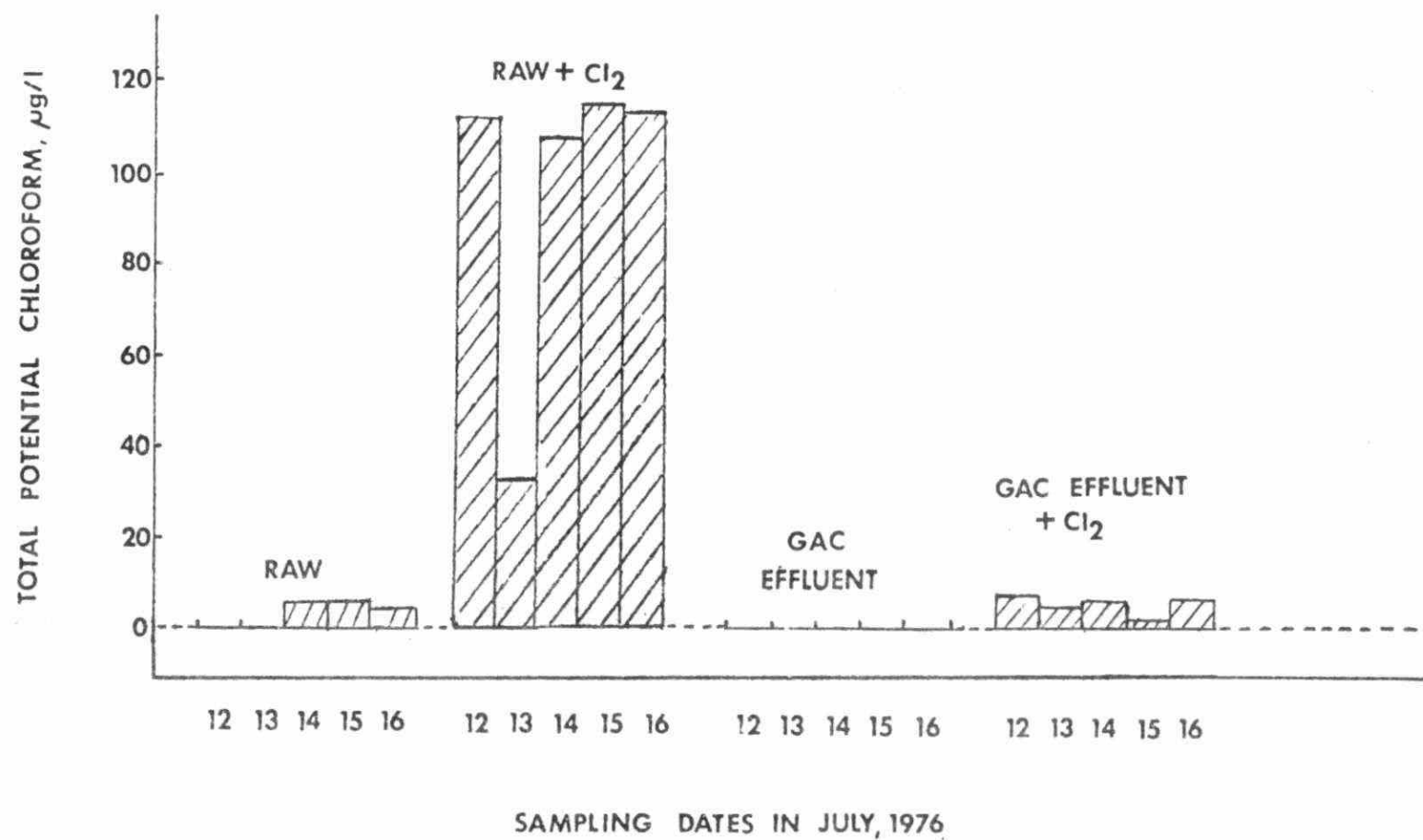


FIGURE 11 REDUCTION OF CHLOROFORM PRECURSORS
IN BELLEVILLE WATER JULY, 1976

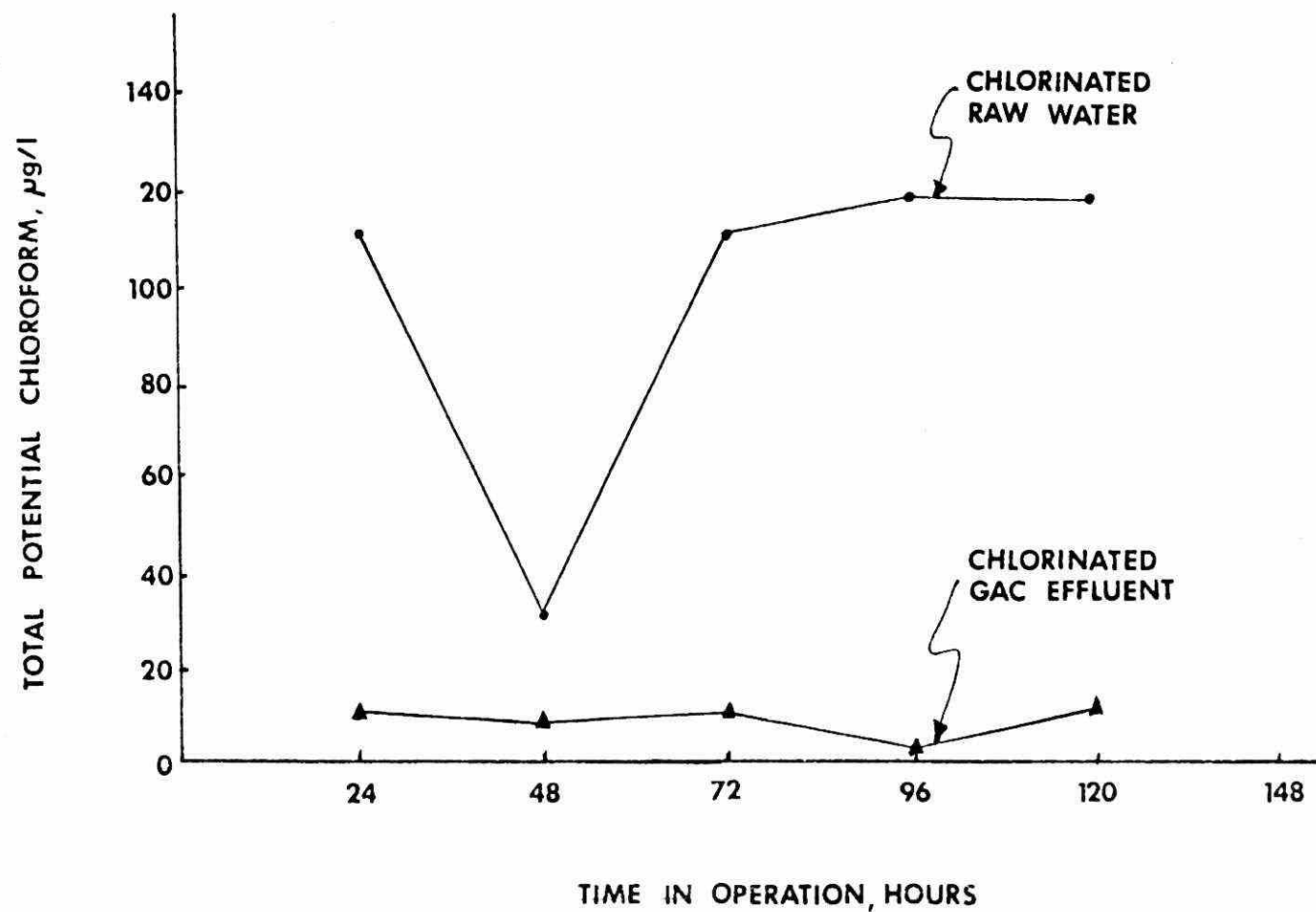


FIGURE 12 ADSORPTION ON GRANULAR ACTIVATED CARBON
FOR REDUCING CHLOROFORM PRECURSORS
IN BELLEVILLE WATER AUGUST, 1976

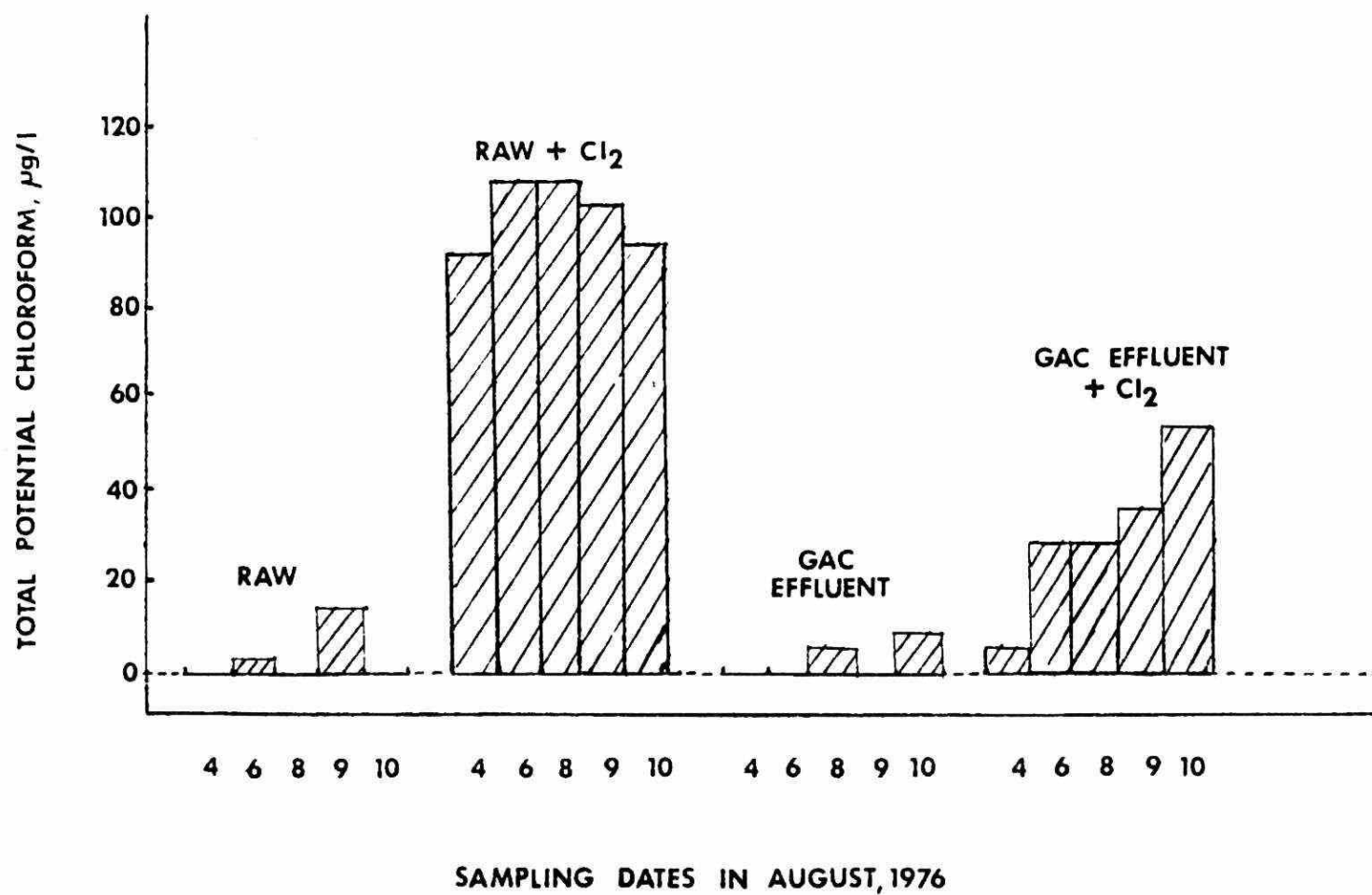


TABLE 12 RESULTS OF THE CHLORINATION OF THE EXTRACTED MATERIALS FROM THE GAC OF THE CAM SAMPLER

	1 ml of CH ₃ OH Solution with Blank GAC Extract			1 ml of CH ₃ OH Solution with CAM Sampler GAC Extract		
	Belleville		Cayuga	Belleville		Cayuga
(1976)	Aug.	July	May	Aug.	July	May
IN 4000 mls MILLIPORE WATER	ND	ND	-	7	ND	-
IN 4000 mls MIL- LIPORE WATER + 1.5 ppm Cl ₂	1	11	-	9	13	-
IN 250 mls MIL- LIPORE WATER	ND	ND	ND	2	2	ND
IN 250 mls MIL- LIPORE WATER + 1.5 ppm Cl ₂	7	14	ND	60	30	20

CH₃OH - methanol

Flash mixing of the coagulants and PAC could probably lead to incorporation of the carbon particles into the floc thereby decreasing the rate of adsorption of organics. This may account for the inconsistent removal patterns of chloroform and its precursors by PAC.

According to the EPA, the trihalomethane concentrations were lowered by 50% when 100 mg/l PAC was used; ⁽¹⁸⁾ such an unrealistically high dosage of PAC is not economically and technologically feasible when applied to actual water treatment plant processes.

Although PAC has been extensively used to remove odours due to its simple application in the water treatment process, the results of this study indicated that any significant advantage in removing the chloroform precursors or chloroform after its was formed, is questionable.

4.4.2 Granular Activated Carbon (GAC)

The adsorption of chloroform precursors on GAC was considered to be effective. Their removal was demonstrated by the results obtained from the CAM Sampler which was run for one week each time. These results were shown in Figures 9 to 12. The raw water temperatures were found to be 15⁰ C for Cayuga water in May, 1976 and 23⁰ C and 22⁰ C for Belleville water in July and August 1976 respectively. A lower chloroform concentration was found in chlorinated CAM Sampler effluents than in the chlorinated raw water. Reductions of chloroform formation from 110 µg/l to 10 µg/l (Figures 10 & 11) and 78 µg/l to 50 µg/l (Figure 9) were obtained in Belleville and Cayuga water respectively. This would account

for 90% and 40% removal of chloroform precursors. The second run of the CAM Sampler at Belleville Water Treatment Plant indicated a 50% removal of chloroform precursors (Figure 12).

The extracted materials from the GAC of the CAM Sampler weighed 0.35 mg per litre of Belleville raw water and 0.38 mg per litre of Cayuga raw water which had passed through the CAM Sampler. An average chloroform level of $26 \mu\text{g/l}$ was obtained in the chlorinated water solution of Belleville which was a mixture of one ml of methanol solution containing the GAC extracted materials and 250 mls of millipore water (Table 12).

The low concentration of chloroform obtained following chlorination of the water solution indicated the incomplete extraction of the chloroform precursors from the carbon and therefore most of the precursors might still remain adsorbed on the carbon. If the extraction of the precursors was complete, then a higher concentration of chloroform would be resulted in the water solution upon chlorination.

Ethanol was used to extract the adsorbed organics. In Germany, dioxane and dimethylformamide were used to extract the carbon and good recovery of the adsorbed organics was obtained.⁽¹⁰⁾ It may have been possible to have had a more complete extraction using dioxane and dimethylformamide.

The CAM Sampler study also showed that when fresh GAC was used, chloroform precursors as well as other organics were adsorbed, thereby reducing the total organic content of the raw water. Low chloroform concentrations could then result in the treated water.

4.4.3 Additional Comments on GAC

The benefits of GAC when it is added to the filter bed in water treatment process can be summarized as follows:-

- 1) Reduction of haloform precursors; amount of haloforms formed upon post-chlorination will be reduced.
- 2) Control of taste and odour problems
- 3) Reduction of other organics in water which limit the formation potential of the by-products of any disinfectant.

However the adsorptive capacity of fresh GAC is limited and after a certain length of time, it will become exhausted. This also depends on the type of GAC used, since carbon prepared from different raw materials or by different activation processes will give different removals for haloforms.⁽¹⁰⁾ Heavier loading of organics and particulates in the raw water would be expected to yield a shorter life for the GAC and thus frequent carbon regeneration would be necessary. The economics of the process become limiting factors here.

An analysis on the costs of using GAC filters in water treatment process to control the formation of haloforms as presented in detail in the Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes published by EPA in June, 1976. Evaluations showed that it is economical to use GAC filters in water treatment plants with a plant capacity greater than $19000 \text{ m}^3/\text{d}$ (5 mgd). Costs of GAC for smaller plants with capacities less than $19000 \text{ m}^3/\text{d}$ (5 mgd) will be extremely high, in the neighbourhood of 40¢/1000 gals, and appear to be unreasonable.

EPA highly recommends the use of GAC as a filter medium in the water treatment process for reducing the production of trihalomethanes. It was one of the regulations proposed by EPA on January 25, 1978 to require the use of GAC filters in many municipalities to purify their waters.⁽¹⁹⁾ The estimated capital expenditures for the plan would be from \$350 million to \$450 million over a three to five year period. However, many water treatment plants in Ontario are comparatively small serving communities of less than 15,000 people. The use of GAC filters seems to be economically practical only for water plants such as Belleville and Brantford with plant capacities around 38,000 m³/d (10 mgd).

5. CONCLUSIONS

Minimizing the concentration of haloform precursors before chlorination was the most effective way of controlling haloform formation in the treated water. Up to 92% removal of haloform precursors was obtained utilizing alum coagulation with activated silica and post-chlorination; as high as 90% removal was also obtained from GAC adsorption. Alum alone was less efficient and alum with polyelectrolytes (anionic, cationic and nonionic) was the least efficient in precursor removal.

The point of chlorination was determined to be very important in minimizing the formation of haloforms; in order to minimize haloforms formation, chlorination should follow coagulation/sedimentation. When pre-chlorination is removed, an alternate disinfectant may be used to alleviate any possible taste and odour production and to provide extended contact. Ozone, potassium permanganate and hydrogen peroxide were tested in this study as alternatives to chlorine in the pre-treatment process. The results showed that these chemicals did not affect the overall performance of alum coagulation with activated silica in haloform precursor removal.

It is postulated that both ozone and hydrogen peroxide oxidized the chloroform precursors to other organic compounds, thus minimizing the chloroform precursor concentration before coagulation/sedimentation and chlorination. Potassium permanganate gave a similar result with Belleville, Brantford and Cayuga water, but there was an immediate increase in haloform precursors upon the treatment of potassium permanganate in Humber River water. The reason for this phenomena is unknown. Although the overall performance of alum coagulation with activated silica in reducing the chloroform precursors was unaffected by these disinfectants, disinfection efficiency and residual effects on growths in the filters and taste and odour removal were not investigated. In addition, further work with regard to the toxicities of their by-products are necessary. Therefore the replacement of chlorine by these disinfectants cannot be determined with the limited data available at present.

Powdered activated carbon was found to be ineffective in reducing the chloroform precursors or the chloroform after it was formed. Adsorption on granular activated carbon was considered to be effective in removing haloform precursors, however its application would require modifications, often not considered economical for existing water treatment plants.

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APPENDIX I

JAR TEST EQUIPMENT

JAR TEST EQUIPMENT

Laboratory jar-tests are used to simulate water treatment process. The data produced depends partially upon the mixing intensity, expressed as the mean velocity gradient, G , which is related to the rotational speed and the configuration of the agitator in addition to the geometry of the mixing vessels.

With the application of Stokes' theory, Camp and Stein ⁽¹⁾ defined the velocity gradient G as:

$$G = \frac{du}{dz} = \sqrt{\frac{W}{U}} = \frac{2\pi ST}{V}$$

where w = power loss per unit volume of liquid
 u = absolute viscosity of the liquid
 S = Rotor speed in rpm
 T = Torque input
 V = Volume of liquid

Three jar-test systems were used in this study. System A had a 1.5 litre square jar with impeller consisted on one blade paddle. System B had a one-litre beaker with a similar type of impeller, whereas System C had a one-litre beaker with a magnetic drive impeller. The diameters of the blades were 7.5 cm, 7.5 cm and 8.7 cm with projected areas of 18.75 cm^2 , 18.75 cm^2 and 17.60 cm^2 for Systems A, B and C respectively. The corresponding G values at 100 rpm for Systems A, B and C were found to be 140 s^{-1} and 54 s^{-1} and 120 s^{-1} respectively according to Lai, Hudson and Singley ⁽²⁾. From their study, it was found that impellers of different shapes but of the same projected areas had the same G values but the different geometries of the mixing vessels resulted in the G values for the three systems. The energy input did not change with the distance of the impellers from the bottom of the vessels. System A with the highest G value was used in this study.

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APPENDIX II

REAGENTS

ALUM

Alum is the coagulant most widely used in Ontario water treatment plants; alum $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ was used as a primary coagulant in this study. A 1% alum solution was prepared by adding 1 mg of powdered alum to 100 mls of distilled water. Alum was applied as 1% solution at the doses of 10, 20, 30, 40 and 50 mg/l. The solution was freshly prepared every two weeks.

POLYELECTROLYTES

The polyelectrolytes Magnifloc 570C (cationic), Magnifloc 847A (anionic) and Magnifloc 971N (non-ionic) supplied by Cyanamid of Canada Ltd., were used as coagulants in this study. These polyelectrolytes were also used as coagulant aids.

The dosages of alum and polyelectrolytes were as follows:-

Alum 1% mg/l	570 C (0.1%)		847 A (0.05%)		971 N (0.5%)	
	as Coag. mg/l	as aid mg/l	as Coag. mg/l	as aid mg/l	as Coag. mg/l	as aid mg/l
20	2.0	2.0	0.2	0.05	0.2	0.05
30	4.0	2.0	0.4	0.2	0.4	0.2
40	6.0	2.0	0.6	0.4	0.6	0.4
50	8.0	2.0	0.8	0.7	0.8	0.7
60	10.0	2.0	1.0	1.0	1.0	1.0

Activated Silica

A 1% activated silica solution was used with the alum coagulant in this study. The solution was freshly prepared every two days. Sodium silicate solution was activated by ammonium sulfate and aged for 5 minutes. The amounts of 1% activated silica solution used were 2 mg/l, 3 mg/l, 4 mg/l, 5 mg/l and 6 mg/l corresponding to 1/10 of

the alum dosages used. They were increased up to 30% of the alum dose later in this study.

POWDERED ACTIVATED CARBON (PAC)

The powdered activated carbon used was pulverized Filtrasorb 200 supplied by Calgon Canada. A 1% PAC slurry was prepared and the dosages used were 5 mg/l and 20 mg/l.

GRANULAR ACTIVATED CARBON (GAC)

The granular activated carbon used was Filtrasorb 200, 14 x 40 mesh, manufactured by Calgon Canada; 70 gms. of GAC was used in the CAM Sampler study.

CHLORINE SOLUTION

The chlorine solution used was prepared by passing chlorine gas through distilled water after circulating through millipore filters. The stock solution was stored in brown glass bottles and stabilized by raising the pH of the solution to 9.5 by a few drops of a 1 N sodium hydroxide solution. 100 mls of the stock solution were diluted and standardized using 0.1 N sodium thiosulfate solution. The chlorine doses used varied with the water being tested; and were determined by free chlorine residuals after two hours. The dosages when averaged were found to be 6 mg/l, 4 mg/l, 6 mg/l and 6 mg/l for water from Belleville, Brantford, Cayuga and Humber River respectively, with a free chlorine residual of 1 mg/l in the test water after two hours contact time.

SODIUM THIOSULFATE SOLUTION, $\text{Na}_2\text{S}_2\text{O}_3$

A 0.1 N solution of sodium thiosulfate was prepared and standardized using 0.02 N potassium dichromate solution before it was used as the inhibitor of chlorine reaction. About 5 drops of the solution were added to the 10 ml samples before they were sent for haloform analysis.

WATER FROM MILLIPORE FILTERS

This is usually known as "millipore water", because it is distilled water having filtered through a series of millipore filters containing granular activated carbon. The water has a low organic content.

OZONE, O_3

Ozone was produced by passing air through a corona generator by utilizing an Alron Portable Water Purifier, Model WP-4. Part of the oxygen was converted to ozone and the mixture of air and ozone (1%) was bubbled through a porous stone diffuser to the water to be tested. The dosage of ozone used was 2 mg/l. The ozonated water was quickly transferred to the jars and the jar test was carried out immediately.

POTASSIUM PERMANGANATE, $KMnO_4$

A 1% potassium permanganate solution was used and the dosage was determined by a preliminary test in which seven jars, each containing one litre of the water to be tested, were dosed with 0.5 mg/l, 1 mg/l, 1.5 mg/l, 3 mg/l, 4 mg/l, 6 mg/l and 8 mg/l of the 1% potassium permanganate solution. The colour of the water was checked after 20 minutes. The dosage which gave the water a brownish-pink colour was determined to be the optimum dosage for pre-treatment.

HYDROGEN PEROXIDE, H_2O_2

A 50% hydrogen peroxide solution supplied by Fischer Scientific Inc. was used in this study. A 2 mg/l dose of the peroxide solution was applied to water to be tested and jar testing was then carried out after 20 minutes.